

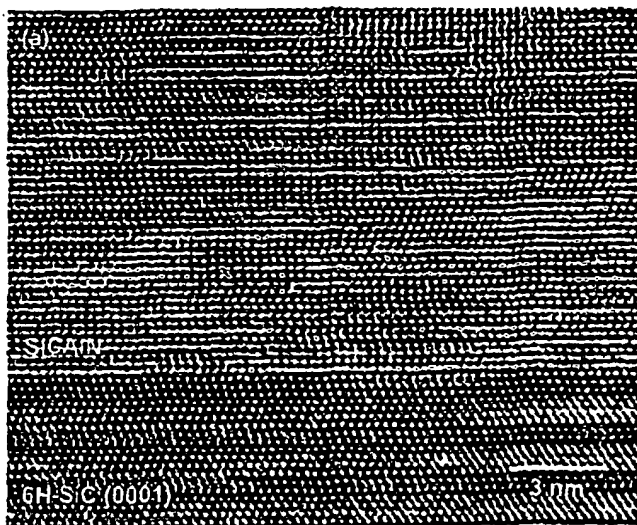
(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
24 April 2003 (24.04.2003)

PCT

(10) International Publication Number
WO 03/033781 A1

- (51) International Patent Classification⁷: C30B 25/00 (74) Agent: MACBLAIN, Thomas, D.; Gallagher & Kennedy, P.A., 2575 East Camelback Road, Phoenix, AZ 85016-9225 (US).
- (21) International Application Number: PCT/US02/33134
- (22) International Filing Date: 16 October 2002 (16.10.2002) (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/981,024 16 October 2001 (16.10.2001) US
60/380,998 16 May 2002 (16.05.2002) US
- (71) Applicant (*for all designated States except US*): ARIZONA BOARD OF REGENTS, a body corporate acting on behalf of Arizona State University [US/US]; Bank One Building, Suite 201, 20 E. University, Tempe, AZ 85282 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): TSONG, Ignatius, S. T. [US/US]; 1445 E. Palomino Drive, Tempe, AZ 85284 (US). KOUVETAKIS, John [US/US]; 7032 E. Indigo, Mesa, AZ 85207 (US). ROUCKA, Radek [CZ/US]; 508 S. Ernie Place, Tempe, AZ 85281 (US). TOLLE, John [US/US]; 1489 South Dove Street, Gilbert, AZ 85233 (US).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: LOW TEMPERATURE EPITAXIAL GROWTH OF QUATERNARY WIDE BANDGAP SEMICONDUCTORS



(57) Abstract: A low temperature method for growing quaternary epitaxial films having the formula XCZ_N wherein X is a Group IV element and Z is a Group III element. A Gaseous flux of precursor H_3XC_N and a vapor flux of Z atoms are introduced into a gas-source molecular beam epitaxial (MBE) chamber to form thin film of XCZ_N on a substrate preferably of silicon or silicon carbide. Silicon substrates may comprise a native oxide layer, thermal oxide layer, AlN /silicon structures or an interface of $Al-O-Si-N$ formed from interlayers of Al on the SiO_2 layer. Epitaxial thin film $SiCA1N$ and $GeCA1N$ are provided. Bandgap engineering is disclosed. Semiconductor devices produced by the present method exhibit bandgaps and spectral ranges which make them useful for optoelectronic and microelectronic applications. $SiCA1N$ deposited on large-diameter silicon wafers are substrates for growth of conventional Group III nitrides such as AlN . The quaternary compounds exhibit extreme hardness.

WO 03/033781 A1

Best Available Copy

LOW TEMPERATURE EPITAXIAL GROWTH OF QUATERNARY WIDE BANDGAP SEMICONDUCTORS

Statement of Government Funding

The U.S. Government through the US Army Research Office provided financial
5 assistance for this project under Grant No. DAAD19-00-1-0471 and through the National
Science Foundation under Grant No. DMR-9986271. Therefore, the United States
Government may own certain rights to this invention.

Cross Reference to Related Applications

This application is related to the following commonly assigned United States patent
10 applications:

1. Serial No. 09/965,022, filed September 26, 2001 in the names of Ignatius S. T.
Tsong, John Kouvetakis, Radek Rouka and John Tolle, entitled "Low Temperature Epitaxial
Growth of Quaternary Wide Bandgap Semiconductors."

2. Serial No. 09/981,024, filed October 16, 2001 in the names of Ignatius S. T.
15 Tsong, John Kouvetakis, Radek Rouka and John Tolle, entitled "Low Temperature Epitaxial
Growth of Quaternary Wide Bandgap Semiconductors." Priority from that application is
claimed herein.

3. Provisional application serial No. 60/380,998 in the names of Ignatius S. T.
Tsong, John Kouvetakis, Radek Rouka and John Tolle entitled "Growth of SiCAIN on Si
20 (111) via a Chrystalline Oxide Interface." Priority from that application is claimed herein.

Each of the aforementioned applications are incorporated herein by reference in their
entirety.

Introduction

Field of Invention

25 This invention concerns a method for forming epitaxial thin films by means of gas
source molecular beam epitaxy (GSMBE). More particularly, this invention relates to a
method for growing high purity, low defect, device quality SiCAIN epitaxial films on silicon
and silicon carbide substrates. SiCAIN films deposited on large diameter silicon wafers also
serve as large-area substrates for Group III nitride growth. Semiconductor films are provided

with bandgaps ranging from 2 eV to 6 eV with a spectral range from visible to ultraviolet, useful for a variety of optoelectronic and microelectronic applications.

Background

Quaternary semiconductors have been sought which incorporate the promising
5 physical and electronic properties of their individual components. Wurtzite AlN and α -SiC have many similar physical properties such as mechanical hardness (1) and thermal expansion (2, 3) as well as closely matched lattice parameters ($a = 3.11\text{\AA}$, $c = 4.98\text{\AA}$ for AlN; $a = 3.08\text{\AA}$, $c = 5.04\text{\AA}$ for 2H-SiC). Both AlN and SiC are well known wide bandgap
10 semiconductors, with wurtzite AlN having a 6.3 eV direct bandgap and 2H-SiC a 3.3 eV indirect bandgap. Quaternary materials are expected to have bandgaps intermediate to those of the constituent binary systems and in some cases the bandgaps may become direct. Thus quaternary compounds offer promise for application in a wide variety of optoelectronic devices.

Early attempts to fabricate ceramic alloys in the quaternary SiC-AlN system by hot-
15 pressing generally involve very high temperatures in the range of 1700 – 2100°C (4, 5). Studies of hot-pressed SiCAlN samples led Zangvil and Ruh (6) to propose a phase diagram showing a flat miscibility gap at 1900°C above which a 2H solid solution of SiCAlN could form. Below 1900°C, the ceramic was found to consist of separate SiC and AlN phases, indicating negligible solubilities between AlN and SiC. The miscibility gap spans from 15 to
20 85 mol % AlN, thus posing likely difficulties for the growth of SiCAlN alloy thin films by conventional techniques at lower temperatures.

Hunter in U.S. Patent Number 6,063,185 discloses methods for producing bulk crystals of SiCAlN which are useful as substrates when sliced into thin wafers for thin film deposition.

25 The epitaxial growth of thin films is one of the major successes in epitaxial techniques such as molecular beam epitaxy (MBE) (7). The growth of metastable structures not available in nature allows the achievement of properties previously unattainable in equilibrium systems.

Solid solutions of AlN and SiC have been grown on vicinal 6H-SiC substrates by
30 MBE at temperatures between 900°C and 1300°C by Kern et al.(8, 9) using disilane (Si_2H_6), ethylene (C_2H_4), nitrogen plasma from an electron cyclotron resonance (ECR) source, and Al evaporated from an effusion cell. The $(\text{SiC})_{1-a}(\text{AlN})_a$ films were shown to be monocrystalline

with a wurtzite (2H) structure for $a \geq 0.25$ and a cubic (3C) structure with $a \leq 0.25$. Jenkins et al. (10) reported the growth of $(\text{SiC})_{1-a}(\text{AlN})_a$ solid solutions with a varying from $a = 0.1$ to $a = 0.9$ using metalorganic chemical vapor deposition (MOCVD) with silane (SiH_4), propane (C_3H_8), ammonia (NH_3) and trimethylaluminum (TMA) in a hydrogen carrier gas. The films were grown on Si(100) substrates at temperatures 1200 – 1250°C and pressures between 10 and 76 Torr. Safaraliev et al. (11) deposited films of $(\text{SiC})_{1-a}(\text{AlN})_a$ on 6H-SiC substrates via the sublimation of sintered SiC-AlN plates at temperatures 1900 – 2100°C. They determined a range of hardness between 20 and 30 GPa for the alloy films. Because of the hardness of the components, it is anticipated that GeCAIN films or coatings and other carbide/nitride quaternary semiconductors comprising Group IV and Group III elements would possess similar superhard properties.

These high temperature synthetic methods, although of research importance, are not suitable for commercial production of SiCAIN or other quaternary thin films comprising Group IV and Group III elements. Methods for growing epitaxial quaternary thin films, especially SiCAIN, under low temperature conditions that are commercially acceptable have been sought. Likewise, other promising epitaxial quaternary semiconductors and methods for depositing them as thin films on substrates useful as semiconductor devices in a wide variety of optoelectronic and microelectronic applications have been sought.

Summary

Accordingly, it is an object of the present invention to provide a low temperature MBE method for the production of epitaxial quaternary semiconducting thin films. Methods for growing low-defect, thin film semiconductors of the general formula $(\text{XC})_{(0.5-a)}(\text{ZN})_{(0.5+a)}$ wherein X is a Group IV element and Z is a Group III element and $0 < a < 0.5$ on a silicon or silicon carbide substrate are provided.

It is a further object of the invention to provide epitaxial quaternary SiCAIN and GeCAIN and other semiconductors produced by the present method. Semiconductor films comprising the quaternary compounds are provided. Such films exhibit bandgaps from about 2 eV to about 6 eV and exhibit a spectral range from visible to ultraviolet which makes them useful for a variety of optoelectronic applications. The quaternary compounds may also be used as a superhard coating material.

These and other objects of the invention are achieved by providing a low temperature

for depositing an epitaxial thin film having the quaternary formula XCZN wherein X is a Group IV element and Z is a Group III element, on a substrate, preferably Si or SiC at temperature between ambient temperature and 1000°C in a gas source molecular beam epitaxial chamber. In the method, a gaseous flux of precursor H₃XCN, wherein H is
5 hydrogen or deuterium, and vapor flux of Z atoms are introduced into the chamber under conditions whereby the precursor and the Z atoms combine to form epitaxial XCZN on the substrate. Most preferably, the temperature is between about 550°C to 750°C. Preferred substrates are Si(111) or α-SiC(0001). In certain preferred embodiments the substrate is a large-diameter silicon wafer. In other preferred embodiments of the present invention X is
10 silicon, germanium or tin. In yet other preferred embodiments Z is aluminum, gallium, indium or boron.

In certain preferred instances of the invention methods are given for depositing thin film XCZN wherein X is silicon and said precursor is H₃SiCN. In other preferred methods the thin film XCZN wherein X is germanium and said precursor is H₃GeCN is given. Most
15 preferably methods are given for depositing epitaxial thin film SiCZN on a substrate wherein the precursor is H₃SiCN, Z atom is aluminum and substrate is Si(111) or α-SiC(0001). In other preferred methods epitaxial thin film GeCZN is deposited on a substrate wherein the precursor is D₃GeCN and substrate is Si(111), Si(0001) or α-SiC(0001)GeCAIN is deposited on the substrate in these methods.

In preferred embodiments of the invention, the substrate comprises a native oxide layer or a thermal oxide layer. In other preferred embodiments, the Si substrate is cleaned, most preferably by hydrogen etching, prior to deposition of the quaternary film. In yet other preferred embodiments, the substrate comprises a buffer layer deposited on the substrate prior to deposition of the quaternary layer. In these embodiments the substrate preferably is
20 Si(111), Si(0001) or α-SiC(0001). A preferred buffer layer is a Group III nitride, most preferably AlN.

In an important aspect of the invention, a crystalline Si-O-Al-N interface is formed on the silicon substrate. In this aspect, a crystalline Si-O-Al-N interface on the silicon substrate is prepared by depositing two or more monolayers of aluminum on the SiO₂ surface of the
30 silicon substrate and the substrate with aluminum monolayers is annealed at a temperature of about 900°C for a period of about 30 minutes prior to the deposition of XCZN. In this method, the SiO₂ surface may be a native oxide layer having a thickness of about 1 nm or a thermally produced oxide layer having a thickness of about 4 nm.

Crystalline Si-O-Al-N interfaces on silicon substrates as substrates for growth of epitaxial film having the formula XCZN wherein X is a Group IV element and Z is a Group III element are presented. A preferred embodiment is SiAlCN epitaxial film grown on a silicon substrate having a Si-O-Al-N interface.

5 In an important aspect of the invention, epitaxial thin films made by the method of the present invention wherein the semiconductor has the quaternary formula XCZN wherein X is a Group IV element and Z is aluminum, gallium or indium, preferably SiCAIN or GeCAIN are presented. These epitaxial thin film semiconductors may be incorporated into optoelectronic and microelectronic devices. Multi-quantum-well structures comprising
10 epitaxial film semiconductor of the present invention, light-emitting diodes and laser diodes comprising multi-quantum well structures are likewise presented. In another preferred embodiment, Z is boron and the film thus-formed is a superhard coating.

In another important aspect of the present invention, a precursor for the synthesis of epitaxial semiconductors having the formula XCZN wherein X is a Group IV element and Z
15 is selected from the group comprising aluminum, gallium and indium, said precursor having the formula H_3XC_N wherein H is hydrogen or deuterium is presented. Again, Z may be boron for production of superhard coatings. In preferred embodiments the precursor is H_3SiCN or H_3GeCN .

In yet another important aspect of the present invention, methods are given for
20 depositing epitaxial thin film having the formula $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$ wherein a is chosen to be a value $0 < a < 0.5$, and Z is the same or different in each occurrence, comprising in addition the step of introducing into said chamber a flux of nitrogen atoms and maintaining the flux of said precursor, said nitrogen atoms and said Z atoms at a ratio selected to produce quaternary semiconductors having said chosen value of x.

25 In preferred instances of this method, a quaternary XCZN semiconductor having a desired bandgap, XC and ZN having different bandgaps and X and Z being the same or different in each occurrence, wherein the flux of precursor, Z atoms and N atoms is maintained at a ratio known to produce a film having the desired bandgap is prepared.

In an important aspect of the invention, epitaxial thin film made by this method and
30 optoelectronic, light-emitting diodes, laser diodes, field emission flat-panel displays and ultraviolet detectors and sensors for example, multi-quantum well structures and microelectronic devices comprising the epitaxial thin film are given.

In yet another important aspect of the present invention, superhard coating made by the method of the present invention are given. Most preferably the coating comprises boron.

The epitaxial thin films made by the method of the present invention that have the formula $XCZN$ wherein X is a Group IV element and Z is a Group III element may be used as substrate for the growth of Group III nitride films, most preferably AlN . The substrate is preferably large-area substrate of $SiCAlN$ grown on large diameter $Si(111)$ wafers by the present method.

In an important aspect of the present invention, layered semiconductor structure made by the present methods and microelectronic or optoelectronic devices comprising a layered semiconductor structure are given.

Brief Description of the Figures

Fig. 1 is a high-resolution cross-sectional transmission electron microscopy (XTEM) image of an epitaxial $SiCAlN$ film grown on α - $Si(0001)$ by the method of the present invention.

Fig. 2 is an X-ray rocking curve of an on-axis $SiCAlN(0002)$ peak of the $SiCAlN$ film illustrated in Fig. 1.

Fig. 3 is an XTEM image showing columnar growth of $SiCAlN$ film grown on $Si(111)$.

Fig. 4 is two XTEM images of a $SiCAlN$ film grown on $Si(111)$. Fig. 4a illustrates the columnar grains, and Fig. 4b illustrates the characteristic ..ABAB.. stacking of the 2H-wurtzite structure of the film.

Fig. 5 illustrates a proposed model of the $SiCAlN$ wurtzite structure. Fig. 5a is a side view of $SiCAlN$ atomic structure and Fig. 5b is a top view of the same structure.

Fig. 6 is an XTEM image of $GeCAlN$ film grown on 6H- $SiC(0001)$ substrate showing epitaxial interface and Ge precipitate.

Fig. 7 is two XTEM images of $GeCAlN$ film grown on $Si(111)$ substrate. Fig. 7a shows a crystalline film with Ge precipitate, and Fig. 7b shows the transition from cubic $Si(111)$ to hexagonal structure of the film at the interface.

Fig. 8 is a Rutherford backscattering (RBS) spectrum of $SiCAlN$ film grown according to the method of the present invention at $725^{\circ}C$. The inset shows the C resonance peak. The RBS simulations giving the atomic compositions of Si, Al, C and N are shown in dashed curves.

Fig. 9 is the Fourier transform infrared spectroscopy (FTIR) spectrum of a $SiCAlN$ film made by the method of the present invention.

Fig. 10a is an electron energy loss spectroscopy (EELS) elemental profile scan of Si, Al, C and N sampled across 35 nm over a SiCAIN film. The region where the 35 nm scan took place on the film is shown as a white line in the lower XTEM image of Fig. 10b.

Fig. 11 illustrates an EELS spectrum showing the K-shell ionization edges of C and N characteristic of sp^3 hybridization of these elements in the SiCAIN film.

Fig. 12 illustrates atomic force microscopy (AFM) images showing the surface morphology of a SiCAIN film grown on SiC(0001). Fig. 12a illustrates an image at Rms: 13.39 nm Ra: 2.84 nm. Fig. 12b is a higher magnification image of the same surface.

Fig. 13 is a diagrammatic illustration of a semiconductor structure comprising the quaternary film semiconductor and a buffer layer on a silicon substrate.

Fig. 14 is a low-resolution XTEM image of the silicon oxynitride interface showing the oxide buffer layer as a thin band of dark contrast adjacent to the interface, as well as the SiCAIN grown above the oxide layer. The arrow indicates the location of the EELS line scan.

Fig. 15 is a EELS compositional profile showing the elemental distribution at the siliconoxynitride interface.

Fig. 16 is a structural model illustrating the transition of the silicon oxynitride interface structure from silica to SiCAIN through an intermediate $Si_3Al_6O_{12}N_2$ framework of a sheet-like structure.

Fig. 17 is a high resolution XTEM of the siliconoxynitride interface showing the converted crystalline oxide buffer layer at the interface. The 2H structure of the SiCAIN is also clearly visible in the upper portion of the film.

Fig. 18 is a diagrammatic illustration of a semiconductor structure having an upper layer of Group III nitride grown on a substrate of SiCAIN or like material.

Detailed Description

While the present invention will be described more fully hereinafter with reference to the examples and accompanying drawings, in which aspects of the preferred manner of practicing the present invention are shown, it is to be understood at the outset of the description which follows that persons of skill in the appropriate arts may modify the invention herein described while still achieving the favorable results of this invention. Accordingly, the description which follows is to be understood as being a broad, teaching

disclosure directed to persons of skill in the appropriate arts, and not as limiting upon the present invention.

This invention provides a low temperature method for growing epitaxial quaternary thin films having the general formulae $XCZN$ wherein X is a Group IV element and Z is a Group III element in a gas source molecular beam epitaxial chamber utilizing gaseous precursors having a structure comprising $X-C-N$ bonds.

An "epitaxial" film generally refers to a film with the highest order of perfection in crystallinity, i.e. as in a single crystal. Because of their low defect density, epitaxial films are especially suitable for microelectronic and, more particularly, optoelectronic applications. The epitaxial growth of unimolecular films is generally achieved in a molecular beam epitaxy (MBE) apparatus. In molecular beam epitaxy (MBE), molecular beams are directed at a heated substrate where reaction and epitaxial film growth occurs. The technology is fully described in E.H.C. Parker (Ed.) "The Technology and Physics of Molecular Beam Epitaxy," Plenum Press (1985) (7). By selecting the appropriate flux species in MBE, and by exercising precise control of the kinetic factors, i.e., flux rate, flux ratio, and substrate temperature, during growth, the morphology, composition and microstructure of films can be tailored on an atomic level.

In the present method, deposition of epitaxial film conforms to a variation of gas-source molecular beam epitaxy (MBE) which comprises a flux of a gaseous precursor and a vapor flux of metal atoms directed onto a substrate where the precursor reacts with the metal atoms to commence growth of epitaxial thin film on the substrate. Typically, the gaseous precursor is connected via a high vacuum valve to the GSMBE chamber (which will be known henceforth as a MBE reaction chamber) containing a heated substrate. Also installed in the MBE reaction chamber is a gas effusion Knudsen cell containing metal atoms. Sources of other vapor flux atoms may also be installed in the chamber. The gaseous precursor is allowed to flow into the reaction chamber which is typically maintained at a base pressure of about 10^{-10} Torr by a ultrahigh vacuum pumping system.

In the present method, the film growth process is conducted in the MBE chamber with the substrate held at temperatures between ambient temperature and 1000°C , preferably in the range of 550°C to 750°C , with flux species consisting of a unimolecular gas-source precursor and elemental atoms from one or more effusion cells. The precursor provides the "backbone" or chemical structure upon which the quaternary compound builds. The substrates are preferably silicon or silicon carbide wafers. In the method, the substrate, growth temperature,

flux species and flux rate may be chosen to determine various features of the quaternary film undergoing growth.

The present method is based on thermally activated reactions between the unimolecular precursor and metal atoms, Z. The molecular structure of the precursor consists of a linear X-C-N skeleton with the target stoichiometry and direct X-C bonds that favor low-temperature synthesis of the quaternary thin film. Any remaining H-X terminal bonds are relatively weak and are eliminated as gaseous H₂ byproducts at low temperatures, making a contamination-free product. The unsaturated and highly electron-rich N site of the C-N moiety has the required reactivity to spontaneously combine with the electron-deficient metal atoms (Z) to form the necessary Z-N bonding arrangements without any additional activation steps.

In the present method, gaseous flux of unimolecular precursor having the formula H₃XCN in vapor form wherein X is a Group IV element, preferably silicon or germanium and H is hydrogen or deuterium is introduced into a GSMBE chamber. A vapor flux of Z atoms, wherein Z is a Group III metal, is also introduced into the chamber from an effusion cell. Pressure and other conditions in the chamber are maintained to allow the precursor and the Z atoms to combine and form epitaxial XCZN on the substrate. Temperature of the substrate during the reaction maintained at a value above ambient and less than 1000°C, considerably below the temperature of the miscibility gap of SiC and AlN phases at 1900°C (6). Most preferably the temperature is maintained between about 550°C to 750°C.

In an important aspect of the method of the present invention, a precursor compound having the formula H₃XCN wherein X is a Group IV element, preferably silicon (Si) or germanium (Ge) and wherein H is hydrogen or deuterium, is provided. The precursor H₃SiCN may be synthesized in a single-step process by a direct combination reaction of SiH₃Br and AgCN. Other suitable methods for preparation of H₃SiCN are known in the art. See, e.g., the method reported by A.G McDiarmid in "Pseudohalogen derivatives of monosilane" Inorganic and Nuclear Chemistry, 1956, 2, 88-94) (12) which involves the reactions of SiH₃I and AgCN. H₃SiCN is a stable and highly volatile solid with a vapor pressure of 300 Torr at 22°C, well suited for the MBE film-growth process. For preparation of quaternary XCZN wherein X is germanium, the precursor D₃GeCN is provided. In these instances, deuterium replaces hydrogen in the precursor to achieve better kinetic stability. The unimolecular precursor GeD₃CN may be synthesized using a direct reaction of GeD₃Cl with AgCN. Other methods for preparation of GeD₃CN utilize GeD₃I as the source of GeD₃

as disclosed in "Infrared spectra and structure of germyl cyanide" T. D. Goldfarb, The Journal of Chemical Physics 1962, 37, 642-646. (13).

In certain instances of the method, the flux rate of metal atom (Z) and precursor are maintained at a rate that provides an essentially equimolar amount of precursor and metal atom to the surface of the substrate i.e., the number of precursor molecules arriving at the substrate surface is the same as the number of metal atoms from the Knudsen effusion cell. In these instances, the quaternary semiconductor that is formed is essentially stoichiometric XCZN and will have the formula $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$ wherein X is a Group IV element and Z is a Group III element and a is essentially zero.

In certain other instances of the method, the stoichiometry of the quaternary compound may be changed by increasing the amount of ZN component. In these instances, extra N-atoms which may be generated by methods known in the art, preferably from a radio frequency (RF) plasma source (also mounted in the MBE chamber) are supplied and the metal (Z) atom flux is increased slightly. The ZN content of the quaternary compound is thus increased to more than 50%, i.e., $a > 0$, as metal atoms Z combine with N in the X-C-N precursor and also with the gaseous N-atoms to form additional ZN. Correspondingly, the XC content will become less than 50%, i.e. drop to $0.5-a$, because $XC + ZN = 100\%$. In these instances, the resultant semiconductor will have the formula $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$ wherein X is a Group IV element and Z is a Group III element and a is between 0 and 0.5.

In an important aspect of the invention, the bandgap of the semiconductors may be adjusted by varying the deposition parameters to create a series of $(XC)_{0.5-a}(ZN)_{(0.5+a)}$ films with different values of a. The bandgap of the quaternary film will reflect the relative concentrations, or stoichiometry of the two components. The composition of the film, i.e. the value of a, can be adjusted by supplying excess C as from CH_4 gas or N as N-atoms from a radio-frequency plasma source. In certain instances, for example when the XC component of the quaternary compound has a different band gap from the ZN component, the flux ratio of precursor, metal atoms and nitrogen atoms may be controlled to increase the amount of ZN in the film and to provide a quaternary film having the desired bandgap.

The bandgap can also be adjusted by changing the constituents, for example, from SiC to GeC or SnC (with calculated bandgaps of 1.6 eV and 0.75 eV respectively). In these instances, the formula of the quaternary compounds will be $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$ wherein X and Z are independently the same or different in each occurrence. Thus a complete series of solid solutions between Group IV carbides and Group III nitrides can be synthesized via the

present method to provide semiconductors with bandgaps ranging from 2 eV to 6 eV, covering a spectral range from infrared to ultraviolet, ideal for a variety of optoelectronic applications. Examples of related novel systems include SiCGaN, SiCInN, GeCGaN, SnCInN and GeCInN.

5 In preferred methods of the present invention, the XCZN quaternary films are grown on semiconductor substrates, preferably Si(111) or α -SiC(0001). Si(100) and Si wafers of other orientations or other material structures may also be used as substrates. The wafers may be cleaned prior to deposition or may comprise buffer layers of oxide or other buffer layers such as Group II nitride, preferably aluminum nitride.

10 In an important aspect of the invention, the deposited XCZN thin film is a substrate for growth of other compounds by methods generally employed in the industry for semiconductor fabrication. Group III nitrides, preferably aluminum nitride, for example, may be grown on SiCAIN thin films prepared by the present method. XCZN films formed on large area wafers comprising Si or SiC are especially suitable for substrates for growth of the
15 Group III nitride layers. This is illustrated diagrammatically in Fig. 18, where 110 is the Si wafer on which the XCZN film 112 is formed and 114 represents a growth of Group III nitride.

Semiconductor quaternary XCZN grown in accordance with the method of the present invention may be doped in order to achieve p-type or n-type material by methods
20 known in the art. The as-deposited SiCAIN films, e.g., are generally of n-type intrinsically. To render the film p-type, dopants known in the art, Mg, for example, may be used.

The hardness of the films prepared by the present method, defined as the applied load divided by the indented surface area, was measured using a nano-indentor (Hysitron Triboscope) attached to an atomic force microscope (AFM). Using the hardness value of 9
25 GPa measured for fused silica as a standard, the nano-indentation experiments yielded an average hardness of 25 GPa for the SiCAIN films, close to that measured for sapphire under the same conditions. The films deposited on silicon substrates are characterized to be true solid solutions of SiC and AlN with a 2H wurtzite structure. The hardness of these films is comparable to that of sapphire. The boron analogues, XCBN are anticipated to be especially
30 suitable as superhard (e.g., 20 GPa or higher) coatings because of the hardness values of the individual binary components.

The present method refers generally to epitaxial growth of nanostructures of quaternary semiconductors on substrate surfaces. Different features of the film surface can

be enhanced, e.g., topography, chemical differences, or work function variations. Thus, in addition to films, quantum wells and quantum dots are provided by the present method.

Superlattice or quantum well structures comprising epitaxial XCZN films of the present invention define a class of semiconductor devices useful in a wide variety of optoelectronic and microelectronic applications. Such devices are useful in high-frequency, high-power, and high-temperature applications including applications for radiation-resistant use. Exemplary of the devices incorporating the wide bandgap semiconductors of the present invention are light-emitting diodes (LED) and laser diodes (LD). Generally, a LED comprises a substrate, α -SiC(0001), Si(111) or Si(111) with AlN buffer layer, and a multi-layer quantum well structure formed on the substrate with an active layer for light emission. In the present instance, the active layer comprises an $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$ (where $0 < a < 0.5$) layer that is lattice-matched with the substrate and prepared by the method of the present invention. Single-phase epitaxial films of a stoichiometric SiCAlN grown at 750°C on 6H-SiC(001) and Si(111) substrates is wide bandgap semiconductor exhibiting luminescence at 390 nm (3.2eV) consistent with the theoretical predicted fundamental bandgap of 3.2eV (15, 22).

Also exemplary of the optoelectronic devices incorporating the present semiconductors are negative electron affinity cathodes for field emission flat-panel displays, high-frequency, high-power, and high-temperature semiconductor devices, UV detectors and sensors.

A large variety of microelectronic and optoelectronic devices comprising semiconductor devices and layered semiconductor structures of the present invention are provided.

Experimental Section

25 Epitaxial XCZN films grown on SiC

Epitaxial SiCAlN films were grown in a MBE chamber according to the present method from the gaseous precursor H_3SiCN and Al atoms from an Knudsen effusion cell supplied to the chamber directly on 6H-SiC (0001) wafer as substrate with the substrate temperature in the region of 550°C to 750°C.

30 In this instance, the α -SiC (0001) wafers were cleaned and surface scratches removed using a process described in U.S. Patent No. 6,306,675 by I.S.T. Tsong et al., "Method for

forming a low-defect epitaxial layer in the fabrication of semiconductor devices," herein incorporated by reference. The base pressure in the MBE chamber was about 2×10^{-10} Torr, rising to about 5×10^{-7} Torr during deposition. The flux rate of each species was set at about $6 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$, giving a $\text{H}_3\text{SiCN:Al}$ flux ratio of ~ 1 and a growth rate at 700-750°C of ~ 4 nm min^{-1} . Films with thickness 130-150 nm were deposited. The deposited films had a transparent appearance as expected for a wide bandgap material.

On the SiC substrates, the epitaxial film shows an ordered hexagonal structure comprising 2H/2H and 4H/2H polytypes² (15). Fig. 12 illustrates atomic force microscopy (AFM) images showing the surface morphology of a SiCAlN film grown on SiC(0001). Fig. 12a illustrates an image at Rms: 13.39nm Ra: 2.84 nm. Fig. 12b is a higher magnification image of the same surface.

Epitaxial XCZN films grown on clean Si(111)

Growth on clean Si(111)-(7X7) substrates, in contrast to the SiC(001) wafers, resulted in inhomogeneous films with a rough surface morphology. TEM studies revealed a microstructure dominated by randomly oriented polycrystalline grains with no significant registry with the underlying Si substrate.

Because of the elimination of the native SiO_2 layer when a crystalline SiCAlN film is grown on a Si(111) substrate, the process of depositing SiCAlN on a large-diameter Si(111) wafer produces a large-area substrate lattice-matched for growth of Group III binary or ternary nitrides such as GaN, AlN, InN, AlGaIn and InGaIn. Large-diameter wafers is a term used in the art to designate wafers larger than about 2 inches.

Epitaxial SiCAlN films grown on Si(111) having a native oxide layer ($\sim 1\text{nm}$)

SiCAlN was deposited by the present method on Si (111) crystals having an intact native oxide layer. In this instance, epitaxial SiCAlN films were grown in a conventional MBE chamber according to the present method, as described hereinabove, directly on Si(111) wafer as substrate with the substrate temperature in the region of 550°C – 750°C.

The microstructure of the films is revealed by a typical XTEM image of the SiCAlN film on Si(111) shown in Figs. 3, 4a and 4b. Columnar grains 25-30 nm wide extending from the film/substrate interface through the entire layer are illustrated by the XTEM image shown in Fig. 3 and 4a. Fig. 3 shows columnar growth of SiCAlN film grown on Si(111), the columns being well-aligned with predominantly basal-plane growth. The randomness in

the orientation of the crystallographic planes in the columns are visible in Fig. 3. Fig. 4 is a pair of XTEM images of a SiCAlN film grown on Si(111). Fig. 4a also illustrates the columnar grains at higher magnification than Fig. 3. Fig. 4b illustrates the characteristic ..ABAB.. stacking. The 2H-wurtzite structure of the film is clearly visible in the high-resolution XTEM images of Fig. 4b. Fig. 5 illustrates a proposed model of the SiCAlN wurtzite structure. Fig. 5a is a side view of SiCAlN atomic structure and 5b is a top view of the same structure.

Growth of single-phase SiCAlN epitaxial films with the 2H-wurtzite structure is conducted directly on Si(Si111) despite the structural differences and large lattice mismatch (19%) between the two materials. Commensurate heteroepitaxy is facilitated by the conversion of native and thermally grown SiO₂ layers on Si(111) into crystalline oxides by in situ reactions of the layers with Al atoms and the H₃SiCN precursor, forming coherent interfaces with the Si substrate and the film. High-resolution transmission electron microscopy (TEM) illustrated in Fig. 17 and electron energy loss spectroscopy (EELS) illustrated in Fig. 15 show that the amorphous SiO₂ films are entirely transformed into a crystalline Si-Al-O-N framework in registry with the Si(111) surface. This crystalline interface acts as a template for nucleation and growth of epitaxial SiCAlN. Integration of wide bandgap semiconductors with Si is readily achieved by this process.

The SiCAlN film was deposited directly on the Si(111) substrate surface with its native oxide layer intact. The EELS spectra of the SiCAlN film obtained with a nanometer beam scanned across the interface show the presence of oxygen. XTEM images of the film/substrate interface show that the amorphous oxide layer has disappeared, replaced by a crystalline interface. It appears that deposition of the SiCAlN film results in the spontaneous replacement of the amorphous SiO₂ layer with a crystalline aluminum oxide layer which in turn promotes epitaxial growth of SiCAlN. Fig. 4b is an XTEM image of SiCAlN grown in Si(111) with a native SiO₂ coating showing the amorphous SiO₂ layer replaced with a crystalline aluminum oxide layer and the epitaxial SiCAlN grown thereon.

Characterization of the deposited films by a variety of spectroscopic and microscopic techniques yielded a near-stoichiometric composition throughout the columnar wurtzite structure with lattice parameters very close to those of 2H-SiC and hexagonal AlN. Transmission electron diffraction (TED) patterns revealed a disordered wurtzite material with lattice constants $a = 3.06\text{\AA}$ and $c = 4.95\text{\AA}$, very close to those of 2H-SiC and hexagonal AlN. Analysis of the films with electron energy loss spectroscopy (EELS) with nanometer beam size showed the uniformity of elemental distribution throughout the SiCAlN film. The EELS

results thus confirm that the film contains a solid solution of SiCAIN. All four constituent elements, Si, Al, C and N, appear together in every nanometer-scale region probed, without any indication of phase separation of SiC and AlN or any segregation of individual elements in the film. A model of the 2H hexagonal structure of SiCAIN is seen in the model in Fig. 5.

5 Growth on the Si(111) with an intact native oxide layer, surprisingly, resulted in transparent crystalline SiCAIN films with significant epitaxial character. High-resolution cross-sectional electron microscopy (XTEM) images of the interface show that the amorphous native oxide was completely converted into a crystalline interface, which acts as a suitable template for nucleation and growth of SiCAIN. However, the limited thickness of
10 the native oxide layer, i.e. ~ 1 nm, made determination of the composition and structure of the interface difficult.

 In experiments involving the native oxide, the as-received Si(111) wafer is used as substrate without prior chemical etching or any other surface preparation or treatment. The crystalline Si-Al-O-N layer can be obtained in situ during film growth at 750°C by a side
15 reaction between the native SiO₂ with the Al flux and N atoms furnished by the H₃SiCN precursor.

 The best results are, however, obtained using a process which involves the deposition of two monolayers of Al on the SiO₂ surface followed by growth of a thin SiCAIN capping layer. Its purpose is to encapsulate the reaction zone thus isolating the Al/SiO₂ assembly to
20 avoid loss of Al and SiO by evaporation during the course of the reaction. The system is annealed at 900°C for 30 minutes. The bulk SiCAIN layer is then grown by reaction of Al and H₃SiCN at 750°C. The flux of each species was $\sim 6 \times 10^{-13}$ cm⁻² s⁻¹ giving a Al/H₃SiCN flux ratio of 1:1. The base pressure of the MBE chamber was 2×10^{-10} Torr rising to 5×10^{-7} Torr during deposition. The growth rate of the SiCAIN was ~ 4 nm per
25 minute. Transparent films with nominal thickness of 150-300 nm were deposited under these conditions.

 The morphology, microstructure and elemental concentration of the films were studied by XTEM and EELS. High resolution XTEM images illustrated in Fig. 17 showed heteroepitaxial growth of 2H-SiCAIN on a coherent and crystalline interface layer. This
30 layer replaces the corresponding amorphous native SiO₂ and acts as compliant template, which presumably accommodates the enormous strain associated with the highly mismatched Si and SiCAIN structures. The EELS elemental profiles shown in Fig. 15 across the interface layer revealed predominately oxygen, aluminum and silicon as well as minor quantities of nitrogen, indicating the presence of a Si-Al-O-N layer grown directly adjacent to the Si

substrate. The oxygen signal decreased rapidly across the thin (~1 nm) interface to background levels in the SiCAlN film. The constituent elements in the SiCAlN layer appeared in every nanoscale region probed at concentrations close to stoichiometric values, consistent with the presence of a SiCAlN film grown on a thin oxynitride interface. The elemental content at the interface was difficult to determine quantitatively since the width of the interface layer, i.e. 1 nm, is comparable to the probe size. Nevertheless EELS provided useful qualitative information with regard to elemental content and showed that the interface layer did not segregate into Al₂O₃ and SiO₂. The near edge fine structure of the Si, Al and O ionization edges indicated a bonding arrangement consistent with a complex Si-Al-O-N phase.

Epitaxial SiCAlN films grown on Si(111) having a thermal oxide layer (~4nm)

SiCAlN film was grown by the methods of the present invention on a Si(111) substrate with a 4-nm thick thermal oxide. The SiCAlN epitaxial thin film were grown using these oxides as buffer layers and compliant templates. The composition and structure of these systems are based on the Si-Al-O-N family of silicon oxynitrides.

To determine the elemental concentrations quantitatively and to investigate the bonding properties of the interface layer, SiCAlN film was grown on Si (111) with a 4-nm thick thermally grown oxide as template. This 4-nm layer thickness is within the resolution of the EELS nanoprobe and is thus more suitable for precise analysis. A pre-oxidized Si(111) substrate with a 4-nm SiO₂ layer is heated at 700°C in UHV to remove any hydrocarbon or other volatile impurities from the surface. The conversion of the amorphous SiO₂ to a crystalline Si-Al-O-N layer follows the procedure described for the native oxide preparation.

Rutherford backscattering spectrometry (RBS) was used to characterize the Si-C-Al-N composition of the films and to detect oxygen and other low level impurities. The 2 MeV spectra indicated that the Si and Al concentrations were 27 and 23 atomic % respectively. Resonant nuclear reactions at 4.27 and 3.72 MeV indicated that the C and N concentrations were 23 - 24 atomic % and 24 - 26 atomic % respectively. Oxygen depth profiles using a resonance reaction at 3.0 MeV did not show any oxygen impurities throughout the bulk SiCAlN layer. However, the data suggested the presence of a thin oxide layer at the Si interface. This indicates the presence of a two-layer heterostructure which consists of a thick SiCAlN film grown on a thin oxide interface. The FTIR spectra showed strong Si-C and Al-N peaks at 740 and 660 cm⁻¹, respectively, corresponding to the SiCAlN bulk film. The

spectra also showed a weak peak at 1100 cm^{-1} which is attributed to Si-O-Al type lattice modes consistent with the presence of the thin oxide layer in the film heterostructure.

Electron microscopy in cross section (XTEM) was used to characterize the microstructure and morphology of the film. Fig. 14 is a typical annular dark-field image showing the SiCAlN film and the underlying oxide layer, visible as a band of darker contrast next to the Si interface. The band is coherent, continuous and fairly uniform with a thickness measured to be about 4 nm, a value close to that of the original SiO₂ layer. Spatially resolved (EELS) with a nanometer size probe was used to examine the elemental concentration across the entire film thickness. The nanospectroscopy showed a homogeneous distribution of Si, C, Al and N throughout the SiCAlN layer, which is consistent with the formation of single-phase alloy material. Analysis across the dark band revealed significant concentrations of oxygen, aluminum and silicon at each nanometer step probed. A typical compositional profile derived from energy-loss line scans (Fig. 15) shows an enhancement of O and Al with a corresponding decrease in Si with respect to SiCAlN. A small concentration of N was also found, as shown in Fig. 15, indicating diffusion of N from the SiCAlN into the interface region presumably during the annealing step. The Carbon content is effectively zero in this region indicating that the interface consists only of Si, Al, O and N. In order to determine quantitatively the composition of the interface region, it is necessary to convolve the effective electron probe distribution with model elemental distributions. This composition profile was modeled as simple step functions at the interface region. The best fit elemental step distributions and corresponding convolved profiles for Si, Al, O and N indicate the presence of a distinct aluminosilicate oxynitride layer with a graded composition yielding an average stoichiometry of Si_{0.14}Al_{0.28}O_{0.50}N_{0.08} over the 4.0 nm thickness. This composition is consistent with known X-silicon phases with stoichiometries ranging from Si₃Al₆O₁₂N₂ (Si_{0.13}Al_{0.26}O_{0.52}N_{0.09}) to the more silica-rich Si₁₂Al₁₈O₃₉N₈ (Si_{0.16}Al_{0.23}O_{0.51}N_{0.10}) (16). X-silicon condenses in a triclinic structure which can be viewed as a distorted hexagonal lattice containing alternating chains of octahedra and tetrahedra linked to form sheets reminiscent of the mullite (Si₂Al₆O₁₃) structure as shown in Fig. 16. In the "low" -X phase of this "nitrogen" -mullite, the edge shared polyhedral sheets in the (100) plane are linked together by tetrahedral AlN₄ and SiO₄ units. A silica-rich "high" -X phase is similar, but possesses a faulted structure.

A typical high-resolution XTEM image of the siliconoxynitride interface heterostructure is shown in Fig. 17, revealing the epitaxial growth of a crystalline interface (buffer layer) which displays a microstructure indicative of a two-dimensional oxide system.

There is a smooth transition between the Si (111) substrate, the interfacial layer and the SiCAIN overlayer. The SiCAIN is highly oriented and exhibits the expected 2H-wurtzite structure, as is clearly visible in the upper portion of the film. The microstructural and nanoanalytical data indicate that the thermal SiO₂ layer has been completely reacted to form a crystalline Si-Al-O-N interface serving as a suitable template for nucleation and growth of SiCAIN.

Growth of crystalline oxide layers directly on Si is a potentially important area of research that remains virtually unexplored. These crystalline oxides possess a wide range of novel properties uniquely suitable for a number of applications such as high- κ gate dielectrics. Development of epitaxial dielectrics on Si has been focused on simple silicates (Sr₂SiO₄) and perovskites (SrTiO₃) (17 - 19). Silicates in the Si_xAl_yO_z system have been previously investigated in reactions of Al with bulk SiO₂ between 550 - 850°C (20, 21). Although no structural and compositional data were provided, these systems were described as homogeneous ternary oxides that exhibit electronic properties similar to those of bulk glasses and zeolites. The inventors' work in this area is believed to represent the first example of a crystalline Si-Al-O-N material, which serves as a buffer layer between Si (111) and tetrahedral semiconductor alloys. These oxynitrides are, in general, high-compressibility (softer) solids compared to either SiCAIN or Si, thereby acting as a soft compliant spacer which can conform structurally and readily absorb the differential strain imposed by the more rigid SiCAIN and Si materials. This elastic behavior may be due to the structure and bonding arrangement consisting of sheet-like edge-shared octahedra and corner-shared tetrahedra which provide a low-energy deformation mechanism involving bond bending forces rather than bond compression forces.

The results of the inventors' work in this area suggest that a complex oxide material is the crucial interface component that promotes epitaxial growth of SiCAIN heterostructures on Si (111). This crystalline oxide is formed by in situ reactions using native and thermal SiO₂ as templates at the Si interface. Integration of wide bandgap nitride semiconductors with Si is readily achieved with the SiCAIN/Si-Al-O-N/Si(111) system serving as an ideal buffer layer. The structural model of Fig. 16 illustrates the transition of the interface structure from silica to SiCAIN through an intermediate Si₃Al₆O₁₂N₂ framework of a sheet-like structure.

Epitaxial XCZN films grown on Si(0001)

Deposition on α -SiC(0001) substrates is virtually homoepitaxy which leads to a low density of misfit and threading dislocations desirable in semiconductors. In those instances wherein silicon is the substrate, a native SiO₂ layer is generally present, and the quaternary film is deposited on the SiO₂ layer. It has been observed that in the present method, the amorphous oxide layer is largely replaced with a crystalline aluminum oxide layer which in turn promotes epitaxial growth of the quaternary film. Fig. 1 illustrates this phenomenon. Fig. 1 is a high-resolution cross-sectional transmission electron microscopy (XTEM) image of an epitaxial SiCAlN film grown on α -Si(0001) by the method of the present invention. Fig. 2 is an X-ray rocking curve of an on-axis SiCAlN(0002) peak of the SiCAlN film illustrated in Fig. 1.

Epitaxial XCZN films grown on Group III nitride buffer layer

In other preferred embodiments of the invention, quaternary epitaxial films were grown on a buffer layer on the silicon substrate. In contrast to growth of SiCAlN on α -SiC(0001) substrates, there may be a large lattice mismatch between the SiCAlN film and the Si(111) substrate. In order to improve epitaxial growth of SiCAlN on Si(111), a buffer layer on Si(111) may be deposited on the Si(111) substrate prior to growth of SiCAlN. The preferred buffer layer is aluminum nitride (AlN). An AlN buffer layer may be deposited by methods known in the art, as, for example, the method disclosed in U.S. Patent No. 6,306,675 by I.S.T. Tsong et al., "Method for forming a low-defect epitaxial layer in the fabrication of semiconductor devices," herein incorporated by reference. Generally, the AlN buffer layer may be deposited through a precursor containing the AlN species or in other instances Al may be provided by evaporation from an effusion cell and combined with N-atoms from a radio-frequency plasma source. Both types of deposition take place in a conventional MBE chamber.

In certain instances, the epitaxial film is deposited on a buffer layer on the silicon substrate. In these instances, the buffer layer provides improved lattice matching for epitaxial growth of the film. Deposition on AlN/Si(111) substrates, for example, is virtually homoepitaxy which leads to a low density of misfit and threading dislocations desirable in semiconductors useful in a variety of optoelectronic and microelectronic applications. Preferred buffer layers are the Group III nitrides, aluminum nitride (AlN), germanium nitride

(GeN), indium nitride (InN), aluminum gallium nitride (AlGaN) and indium gallium nitride (InGaN), most preferably AlN.

Layered semiconductor structures comprising a buffer layer and a quaternary epitaxial film having the formula XCZN deposited on the layer are provided. Fig. 13 illustrates a model of a layered semiconductor structure 10 comprising semiconductor quaternary film XCZN 106, buffer layer 104 and substrate silicon or silicon carbide 102.

GeCAIN Thin Films

Other preferred embodiments of the present invention provide a method for preparing epitaxial quaternary films of the formula GeCZN wherein Z is a Group III element. Epitaxial quaternary films of the formula GeCZN wherein Z is aluminum, gallium or indium or, in certain instances, transition metals, are also wide bandgap semiconductors and are an alternative optoelectronic material to SiCAIN because of the theoretical bandgap of 1.6 eV for GeC (14).

Quaternary GeCAIN compounds are prepared by the present method by providing the precursor D_3GeCN . A flux of gaseous precursor, unimolecular D_3GeCN molecules, and vapor flux of Al atoms are introduced into the GSMBE chamber maintained at a pressure whereby the precursor and Al atoms combine to form epitaxial GeCAIN thin film the substrate. Temperature during the reaction is less than 1000°C, most preferably between about 550°C to 750°C. Substrate is silicon, preferably Si (111) or α -SiC(0001). In certain other instances, a transition metal, Ti, or Zr, e.g., may be supplied from an effusion cell to form a series of quaternary compounds of different metal atoms.

The microstructures of GeCAIN films deposited at 650°C on Si and SiC substrates are shown in XTEM images in Figs. 6 and 7. Fig. 6 is an XTEM image of GeCAIN film grown on 6H-SiC(0001) substrate showing epitaxial interface and Ge precipitate. Fig. 7a shows a crystalline film with Ge precipitate, and Fig. 7b shows the transition from cubic Si(111) to hexagonal structure of the film at the interface. The diffraction data indicate that this material consists of cubic Ge particles and disordered hexagonal crystals containing all the constituent elements, Ge, Al, C and N, according to EELS analyses. RBS analyses revealed that while the Al, C and N contents are nearly equal, the Ge concentration is substantially higher than the ideal 25 % value. Similar to the growth of SiCAIN on Si(111) substrates with intact native oxide layers, the XTEM images of GeCAIN/Si interfaces are as depicted in Fig. 7.

This shows a clear transition from cubic structure of the substrate to hexagonal structure of the film without the amorphous oxide layer.

Analysis and Characterization of epitaxial quaternary films grown by the method of the present invention.

5 A detailed characterization of the present quaternary XCZN films was provided by a thorough analysis utilizing a variety of techniques. The films may be more thoroughly understood in accordance with the Figs. and with the results given in the following subsections entitled: (1) Composition determined by Rutherford backscattering analysis; (2) Fourier transform infrared spectroscopy (FTIR); (3) Cross-sectional transmission electron
10 microscopy (XTEM); (4) Transmission electron diffraction (TED); (5) Energy loss spectroscopy (EELS); (6) Bandgap measurements; (7) Surface Morphology; and (8) Hardness measurements.

(1) Composition of SiCAIN films determined by Rutherford backscattering (RBS)

Rutherford backscattering spectrometry (RBS) was used to determine the elemental
15 composition, detect H and O impurities, and estimate the film thickness. The Si and Al elemental concentrations of each film were measured at 2 MeV, and resonant nuclear reactions at 4.27 MeV and 3.72 MeV were used to determine the C and N contents respectively. Results of this analysis are illustrated in Fig. 8.

The C and N concentrations in most films were nearly equal, at 23-24 at. % and 24-26 at. %
20 respectively, suggesting that the entire C-N unit of the precursor was incorporated into the film. The Al concentration in all films was 21-23 at. %, consistent with the high affinity of Al for the N ligand, but always slightly lower than that of C and N. The Si content for all films was measured at 27-29 at. %, consistently higher than the ideal 25 at. %. Typical compositions of the SiCAIN films determined by RBS lie in the following range: Si 27-29
25 atomic %, Al 21-23 atomic %, C 23-24 atomic %, and N 24-26 atomic %. The Si content is consistently higher than the stoichiometric 25 atomic %. This anomaly can be attributed to a minor loss of C-N during deposition of the precursor. Alternatively, the replacement of weaker Al-C bonding (which is present in an ideally stoichiometric SiCAIN solid solution) by stronger Si-C bonding at some lattice sites may account for the excess Si over Al. Oxygen
30 resonance at 3.05 MeV confirmed the absence of any measurable O impurities in the bulk. Forward recoil experiments showed only background traces of H, indicating the complete elimination of H ligands from the precursor during growth. Depth profiling by secondary ion

mass spectrometry (SIMS) showed homogeneous elemental distribution throughout and confirmed the absence of O and other impurities.

(2) Fourier transform infrared spectroscopy of SiCAlN films (FTIR)

Fourier transform infrared spectroscopy (FTIR) in the transmission mode was used to
5 examine the bonding properties of the constituent elements in all films. Results are
illustrated in Fig. 9. The FTIR spectrum shows two broad peaks at wavenumbers 740 cm^{-1}
and 660 cm^{-1} corresponding to Si-C and Al-N lattice vibrations respectively. These
wavenumbers are significantly lower than those of pure Si-C (800 cm^{-1}) and pure Al-N (690 cm^{-1}), consistent with the formation of an extended alloy between the two binary systems. A
10 lower intensity peak is also observed at 600 cm^{-1} and is assigned to Al-C type lattice
vibrations. Bands between $800 - 900\text{ cm}^{-1}$ are assigned to Al-C type lattice vibrations.
Bands between $800 - 900\text{ cm}^{-1}$ which would correspond to Si-N stretching absorptions are
not clearly resolved in the spectrum in Fig. 9. However, their presence cannot be ruled out
because it is likely that they overlap with the broad onset of the Si-C absorption. The
15 spectrum in Fig. 9 does not show any additional peaks attributable to Si-H vibrations between
 $2200 - 2100\text{ cm}^{-1}$, confirming the elimination of the H ligand from the precursor.

Absorption spectra taken from Fourier transform infrared spectroscopy (FTIR) show
major peaks due to Si-C and Al-N lattice vibrations and minor peaks due to Al-C and Si-N
vibrations, in agreement with the wurtzite structure and chemical bonding of the SiCAlN
20 film.

(3) Cross-sectional transmission electron microscopy

The microstructure of the films was studied by cross-sectional transmission electron
microscopy (XTEM). A typical high-resolution XTEM image of the epitaxial growth of
SiCAlN on an α -SiC(0001) substrate is shown in Fig. 1. The characteristic ...ABAB..
25 stacking of the 2H wurtzite structure is clearly visible in the grains of the film shown in Fig.
1. A model atomic structure proposed for the SiCAlN epitaxial film is shown in Fig. 5. A
typical XTEM image of a SiCAlN film grown on a Si(111) substrate is shown in Figs. 3 and
4a revealing columnar grains $\sim 25\text{ nm}$ wide extending from the film/substrate interface
through the entire layer. The XTEM images of the SiCAlN film grown on Si(111) include
30 some columnar grains with a-lattice planes oriented normal instead of parallel to the interface
(Fig. 3).

(4) Transmission electron diffraction

Transmission electron diffraction (TED) patterns of SiCAlN films give lattice constants of $a = 3.06 \text{ \AA}$ and $c = 4.95 \text{ \AA}$, very close to those of 2H-SiC and hexagonal AlN. Transmission electron diffraction (TED) patterns indicate a disordered wurtzite material with lattice constants $a = 3.06 \text{ \AA}$ and $c = 4.95 \text{ \AA}$, very close to those of 2H-SiC and hexagonal AlN. A survey of digital diffractograms of the lattice fringes indicates that the lattice spacings are constant throughout the grains, and close to the values obtained from TED patterns.

(5) Energy loss spectroscopy of SiCAlN films

Electron energy loss spectroscopy (EELS) with nanometer beam size was used to study the uniformity of elemental distribution throughout the film. Typical elemental profiles scanned across the columnar grains in the film are shown in Fig. 10 which is an EELS elemental profile scan of Si, Al, C and N sampled across 70 nm over a SiCAlN film showing the distribution of all four constituent elements. The corresponding RBS atomic concentrations for Si, Al, N, and C are 29, 21, 26, and 24 at. % respectively. The lower C content detected by EELS is due to preferential depletion of C from the lattice sites by the electron beam. The region where the scan took place on the film is shown as a white line in the lower XTEM image

All four constituent elements, Si, Al, C and N, appear together in every nanometer-scale region probed, without any indication of phase separation of SiC and AlN or any segregation of individual elements in the film.

The EELS results are accurate to within 10 at. % and thus confirm that the film contains a solid solution of SiCAlN. The minor elemental variations observed in Fig. 10 may be due to compositional inhomogeneity across grain boundaries. While the EELS elemental concentrations for N, Al, and Si in all samples are close to those obtained by RBS (certainly within the 10 % error associated with the technique) the EELS elemental concentration of C is consistently lower by a significant amount than the RBS value. This is due to the preferential depletion of C from the lattice sites by the finely focused intense electron beam. An EELS spectrum featuring K-shell ionization edges representing the σ^* transition for both C and N is shown in Fig. 11. Peaks corresponding to π^* transitions characteristic of sp^2 hybridization are not observed at these edges, indicating the absence of sp^2 hybridized carbon and related planar C-N networks generally associated with the decomposition of the unimolecular

precursor. The EELS spectrum thus confirms that both C and N are sp^3 hybridized and tetrahedrally coordinated as in SiC and AlN.

(6) Bandgap measurements

Optical absorption experiments suggest that the bandgap for the SiCAlN epitaxial film is no less than 3.8 eV, as would be expected from the bandgaps of the constituents SiC (3.3 eV) and AlN (6.3 eV). The direct bandgap of the SiCAlN films may be observed by vacuum ultraviolet (VUV) ellipsometry.

(7) Surface Morphology

Atomic force microscope images illustrated in Fig. 12a and 12b show a relatively smooth as-grown surface of a SiCAlN thin film grown according to the method of the present invention. The complete lack of facets on the as-grown surface indicates that the predominant growth direction is basal-plane, i.e. (0001), oriented.

(8) Hardness measurements

The SiCAlN solid solution films can also serve as superhard coatings for protection of surfaces against wear and erosion. The hardness of the films was measured using a Hysitron Triboscope attached to a Digital Instruments Nanoscope III atomic force microscope. The hardness in this case is defined as the applied load divided by the surface area of the impression when a pyramidal-shaped diamond indenter is pressed normally into the film surface. Using the hardness value of 9 GPa measured for fused silica as a standard, the indentation experiments yielded an average hardness of 25 GPa for the SiCAlN films, close to that measured for sapphire under the same experimental conditions. The reported Vickers hardness for SiC and AlN are 28 ± 3 and 12 ± 1 GPa, respectively (1).

Those skilled in the art will appreciate that numerous changes and modifications may be made to the preferred embodiments of the invention and that such changes and modifications may be made without departing from the spirit of the invention. It is therefore intended that the appended claims cover all such equivalent variations as fall within the true spirit and scope of the invention.

References

1. Teter, D M, MRS Bulletin 23(1), 22 (1998).
2. Moroc, H, Strite, S, Gao, G B Lin, M E, Sverdlov B., Burns, M, J Appl. Phys. 76, 1363 (1994).
- 5 3. Tanaka, S, Kern R S, Davis R, Appl. Phys. Lett. 66, 37 (1995).
4. Ruh R, Zangvil, A, J. Am. Ceram. Soc. 65, 260 (1982).
5. Rafaniello, W, Plichta, M R, Virkar, A V, J. Am. Ceram. Soc 66, 272 (1983).
6. Zangvil, A, Ruh, R, J. Am. Ceram. Soc 71, 884 (1988).
7. Parker E.H.C(Ed.), "The Technology and Physics of Molecular Beam Epitaxy"
- 10 Plenum Press (1985).
8. Kern, R S, Rowland, L B, Tanaka, S, Davis, R F, J. Mater. Res. 8, 1477 (1993).
9. Kern, R S, Rowland, L B, Tanaka, S, Davis, R F, J. Mater. Res. 13, 1816 (1998).
10. Jenkins, I, Irvine, K G, Spencer, M G, Dmitriev, V, Chen, N J, Cryst. Growth 128, 375 (1993).
- 15 11. Safaraliev, G K, Tairov, Yu M, Tsvetkov, V,F, Sov. Phys. Semicond. 25, 865 (1991).
12. McDiarmid, A G, Inorganic and Nuclear Chemistry, 1956, 2, 88-94.
13. Goldfarb, T D, The Journal of Chemical Physics 1962, 37, (642-646.).
14. Pandey, R, Rerät, M, Darrigan, C, Causa, M, J. Appl. Phys. 88, 6462 (2000).
15. Roucka, R, Tolle, J, Chizmeshya, A V G, Crozier, P A, Powelieit, C D, Smith, D J,
- 20 Tsong, I S T and Kouvetakis, J Phys. Rev. Lett. (in press).
16. Schmucker, M and Schneider, H, J. Am. Ceeram. Soc. 82, 1934 (1999).
17. Liang, Y, Gan, S and Engelhard, M, Appl. Phys. Lett. 79, 3591 (2001).
18. McKee, R A, Walker, F J and Chisholm, M F, Phys. Rev. Lett. 81, 3014 (1998).
19. Yu, S, Ramdani, J, Finder, J M, Overgard, C D, Corner, J R and Kaushik, V S, J. Vac.
- 25 Sci. Technol. B18, 1653 (2000).
20. Anandan, C, Appl. Surf. Sci. 89, 57 (1995).
21. Grundling, C, Lercher, J A and Goodman, D W, Surf. Sci. 318, 97 (1994).
22. Roucka, R, Tolle, J, Smith, D J, Crozier, P, Tsong, I S T and Kouvetakis, J, Appl. Phys. Lett. 79, 2880 (2001).

We claim:

- 1 1. A method for depositing an epitaxial thin film having the quaternary formula
2 XCZN, wherein X is a Group IV element and Z is a Group III element, on a substrate at a
3 temperature between ambient temperature and 1000°C in a gas source molecular beam
4 epitaxial chamber, comprising introducing into said chamber:
5 (a) a gaseous flux of a precursor H_3XCN , wherein H is hydrogen or
6 deuterium;
7 and
8 (b) a vapor flux of Z atoms;
9 whereby said precursor and said Z atoms combine to form epitaxial XCZN on
10 said substrate.
- 1 2. The method of claim 1, wherein said temperature is about 550°C to 750°C.
- 1 3. The method of claim 1, wherein said substrate is silicon or silicon carbide.
- 1 4. The method of claim 3, wherein said substrate is Si(111), Si(0001) or α -
2 SiC(0001).
- 1 5. The method of claim 3, wherein said substrate is a large-diameter silicon
2 wafer.
- 1 6. The method of claim 3, wherein said substrate has thereon an oxide layer onto
2 which the epitaxial thin film is deposited.
- 1 7. The method of claim 1, further comprising the step of cleaning said substrate
2 prior to deposition of said quaternary film.
- 1 8. The method of claim 7, wherein said cleaning step comprises hydrogen
2 etching.
- 1 9. The method of claim 5, wherein said substrate is Si(111), Si(0001) or α -
2 SiC(0001).
- 1 10. The method of claim 1, further comprising depositing a buffer layer on said
2 substrate prior to deposition of said quaternary film.

- 1 11. The method of claim 10, wherein said substrate is Si(111), Si(0001) or α -
2 SiC(0001).
- 1 12. The method of claim 10, wherein said buffer layer is a Group III nitride.
- 1 13. The method of claim 12, wherein said buffer layer is AlN.
- 1 14. A layered semiconductor structure made by the method of any one of claims 1
2 - 13.
- 1 15. A microelectronic or optoelectronic device comprising the layered
2 semiconductor structure of claim 14.
- 1 16. The method of claim 1, wherein X is silicon, germanium or tin.
- 1 17. The method of claim 1, wherein Z is aluminum, gallium or indium.
- 1 18. The method of claim 1, wherein Z is boron.
- 1 19. The method of claim 1, for depositing thin film XCZN, wherein X is silicon
2 and said precursor is H_3SiCN .
- 1 20. The method of claim 1, for depositing the thin film XCZN, wherein X is
2 germanium and said precursor is H_3GeCN .
- 1 21. The method of claim 1, for depositing epitaxial thin film SiCZN on a
2 substrate, wherein said precursor is H_3SiCN , the Z atoms are aluminum and the substrate is
3 Si(111), Si(0001) or α -SiC(0001).
- 1 22. The method of claim 1, for depositing epitaxial thin film GeCZN on a
2 substrate, wherein said precursor is D_3GeCN , the Z atoms are aluminum and the substrate is
3 Si(111), Si(0001) or α -SiC(0001).
- 1 23. An epitaxial thin film having the formula XCZN, wherein X is a Group IV
2 element and Z is a Group III element or a transition metal, made by the method of any one of
3 claims 1 - 13.

- 1 24. The method according to claim 6, wherein the oxide layer is of a native oxide.
- 1 25. The epitaxial thin film semiconductor made by the method of any one of
2 claims 1 - 13, said semiconductor having the quaternary formula $XCZN$, wherein X is a
3 Group IV element and Z is boron, aluminum, gallium or indium.
- 1 26. An optoelectronic device comprising the epitaxial thin film semiconductor of
2 claim 25.
- 1 27. The optoelectronic device of claim 26, wherein said semiconductor is SiCAIN
2 or GeCAIN.
- 1 28. A microelectronic device comprising the epitaxial thin film semiconductor of
2 claim 25.
- 1 29. The microelectronic device of claim 28, wherein said semiconductor is
2 SiCAIN or GeCAIN.
- 1 30. A multi-quantum-well structure, comprising an epitaxial film semiconductor
2 of claim 25.
- 1 31. A light-emitting or laser diode comprising the multi-quantum well structure
2 of claim 30.
- 1 32. The method of any one of claims 1 - 13, for depositing epitaxial thin film
2 having the formula $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$, wherein a is chosen to be a value $0 < a < 0.5$, and Z is
3 the same or different in each occurrence, comprising in addition the step of introducing into
4 said chamber a flux of nitrogen atoms and maintaining the flux of said precursor, said
5 nitrogen atoms and said Z atoms at a ratio selected to produce quaternary semiconductors
6 having said chosen value of a.
- 1 33. An epitaxial thin film made by the method of claim 32.
- 1 34. An optoelectronic device comprising the epitaxial thin film of claim 33.
- 1 35. A microelectronic device comprising the epitaxial thin film of claim 33.
- 1 36. A superhard coating made by the method of any one of claims 1 - 13.

1 37. The superhard coating of claim 36, wherein Z is boron.

1 38. An epitaxial thin film made by the method of any one of claims 1 - 13, the
2 film being a substrate for a layer of Group III nitride thereon, and the film having the formula
3 XCZN, wherein X is a Group IV element and Z is a Group III element.

1 39. The method of claim 32 for producing a quaternary XCZN semiconductor
2 having a desired bandgap, XC and ZN having different bandgaps and X and Z being the same
3 or different in each occurrence, wherein the flux of precursor, Z atoms and nitrogen atoms is
4 maintained at a ratio predetermined to produce a film having the desired bandgap.

1 40. A multi-quantum-well structure comprising the epitaxial film of claim 39.

1 41. A light-emitting or laser diode comprising the multi-quantum well structure
2 of claim 40.

1 42. An optoelectronic device comprising a semiconductor made by the method of
2 claim 37.

1 43. An optoelectronic device of claim 42, selected from the group consisting of
2 light-emitting diodes, laser diodes, field emission flat-panel displays and ultraviolet detectors
3 and sensors.

1 44. The method of claim 1, wherein the substrate has thereon a SiO₂ surface, the
2 method further comprising the steps of:

3 (c) depositing a plurality of monolayers of Al on the SiO₂ surface; and

4 (d) annealing the deposited Al monolayers prior to the deposition of

5 XCZN.

1 45. The method of claim 44 for preparing a crystalline Si-O-Al-N interface on the
2 silicon substrate.

3 46. The method of claim 44, wherein the SiO₂ surface is native oxide layer having
4 a thickness of about 1 nm.

1 47. The method of claim 44, wherein the SiO₂ surface is a thermally produced
2 oxide layer, r having a thickness of about 4 nm.

1 48. Large-area substrate for the growth of Group III nitride film, the substrate
2 being of SiCAlN grown on large diameter Si(111) wafers by the method of any one of claims
3 1 - 13.

1 49. The substrate of claim 45, wherein said Group III nitride film is AlN.

1 50. A precursor for the synthesis of epitaxial semiconductors having the formula
2 XCZN, wherein X is a Group IV element and Z is selected from the group comprising boron,
3 aluminum, gallium and indium, said precursor having the formula H_3XCN wherein H is
4 hydrogen or deuterium.

1 51. The precursor of claim 50, having the formula H_3SiCN .

1 52. The precursor of claim 50, having the formula H_3GeCN .

1 53. A crystalline Si-O-Al-N interface on silicon substrate as a substrate for growth
2 of epitaxial film having the formula XCZN wherein X is SiAlCN epitaxial film grown on a
3 silicon substrate having a Si-O-Al-N interface.

1 54. An epitaxial thin film substrate for a layer of Group III nitride thereon, the
2 film having the formula XCZN, wherein X is a Group IV element and Z is a Group III
3 element.

1 55. A semiconductor structure comprising a semiconductor substrate and a layer
2 deposited on the substrate of a material of the formula XCZN, where X is a Group IV
3 element and Z is a Group III element.

1 56. A wide bandgap semiconductor of the formula XCZN, where X is a Group IV
2 element and Z is a Group III element.

1 57. The semiconductor of claim 56, wherein the bandgap of said semiconductor is
2 from about 2eV to about 6eV.

1 58. A semiconductor structure comprising a semiconductor substrate and a layer
2 deposited on the substrate of a material having the formula $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$, where X is a
3 Group III element, Z is a Group IV element, and $0 < a < 0.5$.

1 59. A wide bandgap semiconductor of the formula $(XC)_{(0.5-a)}(ZN)_{(0.5+a)}$ where -x
2 is a Group III element, Z is a Group IV element and $0 < a < 0.5$.

1 60. A semiconductor structure comprising a substrate of semiconductor material, a
2 layer of crystalline oxide of the semiconductor material on a surface of the substrate and a
3 layer of material having the formula XCZN on the crystalline oxide layer, where X is a
4 Group IV element and Z is a Group III element.

1 61. The semiconductor structure according to claim 60, wherein the semiconductor
2 material is Si and the oxide is SiO_2 .

1 62. The semiconductor structure according to claim 60, wherein the oxide is less
2 than ten monolayers thick.

1 63. The semiconductor structure according to claim 62, wherein the oxide is two
2 monolayers thick.

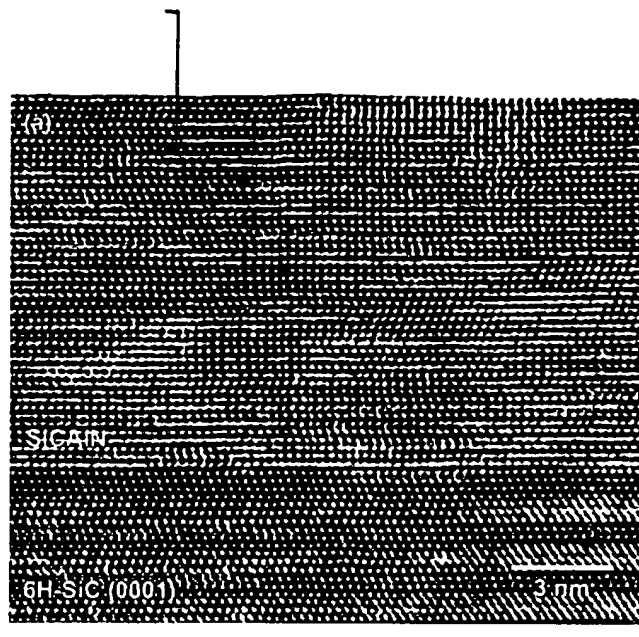
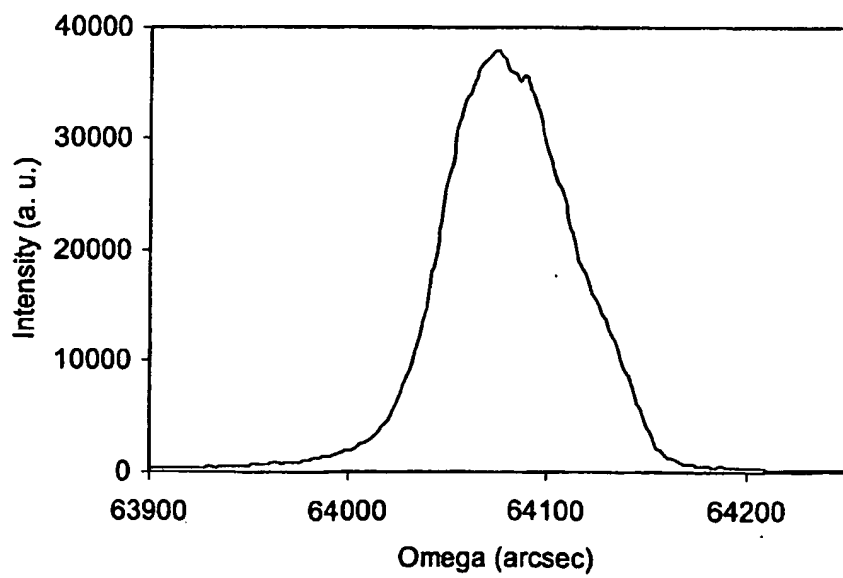
**Fig. 1****Fig. 2**



Fig. 3

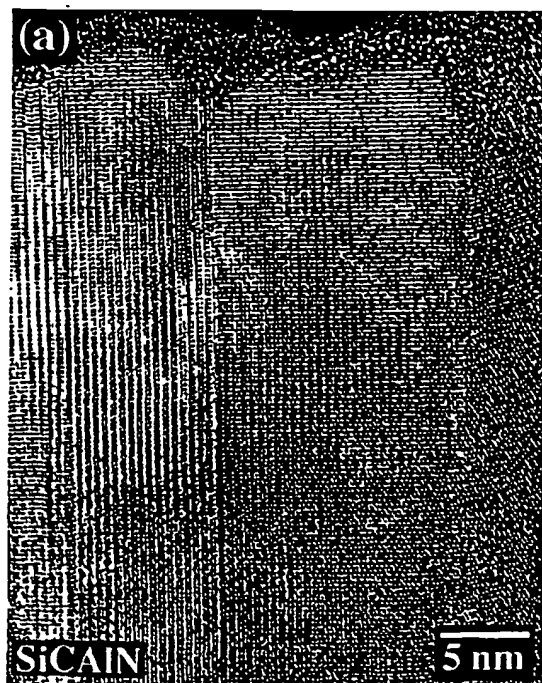


Fig. 4a

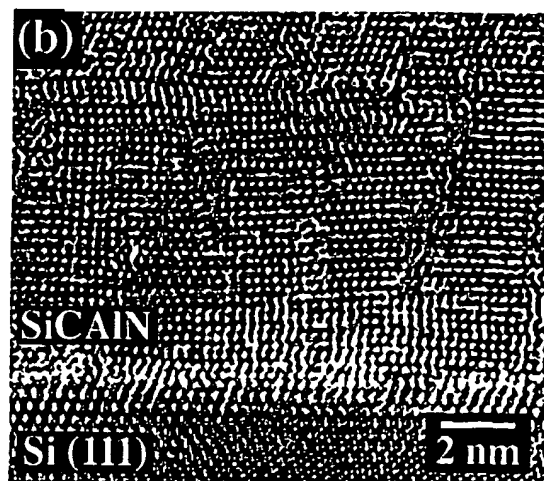


Fig. 4b

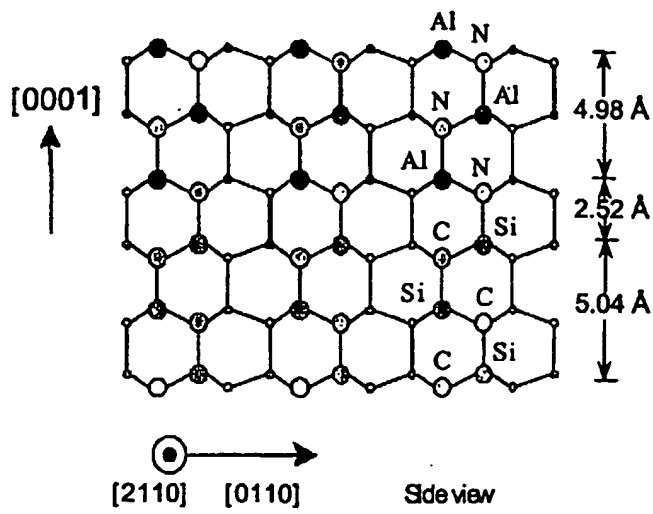


Fig. 5a

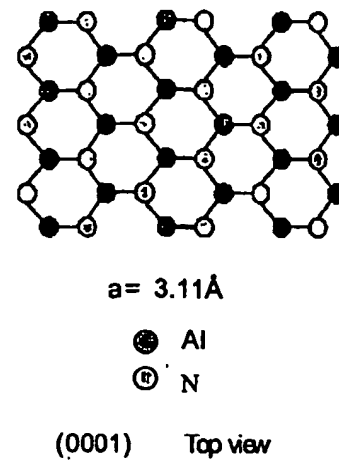


Fig. 5b

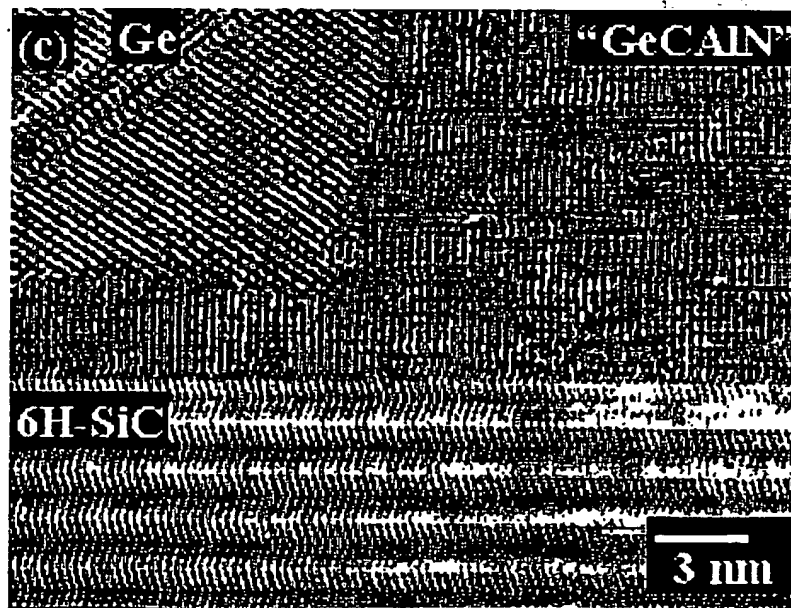


Fig. 6

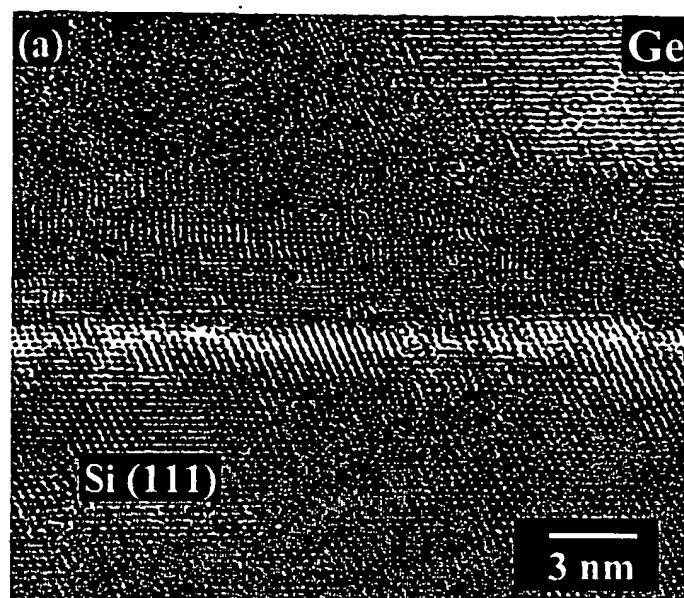


Fig. 7a

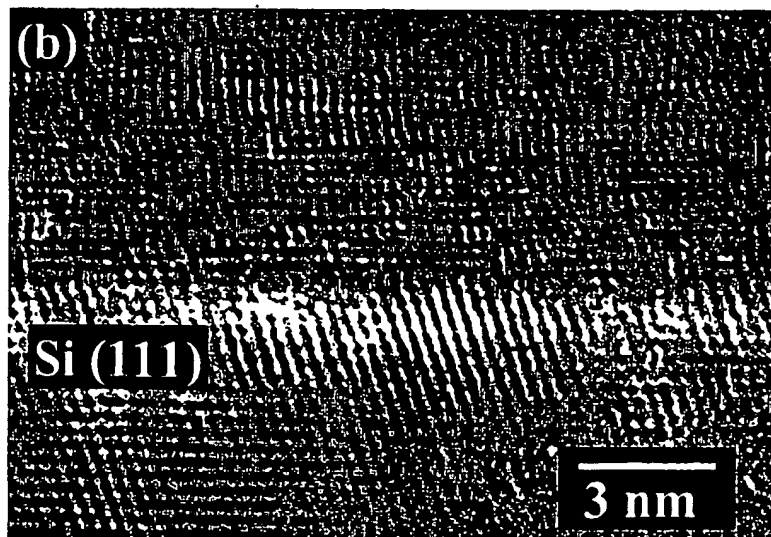


Fig. 7b

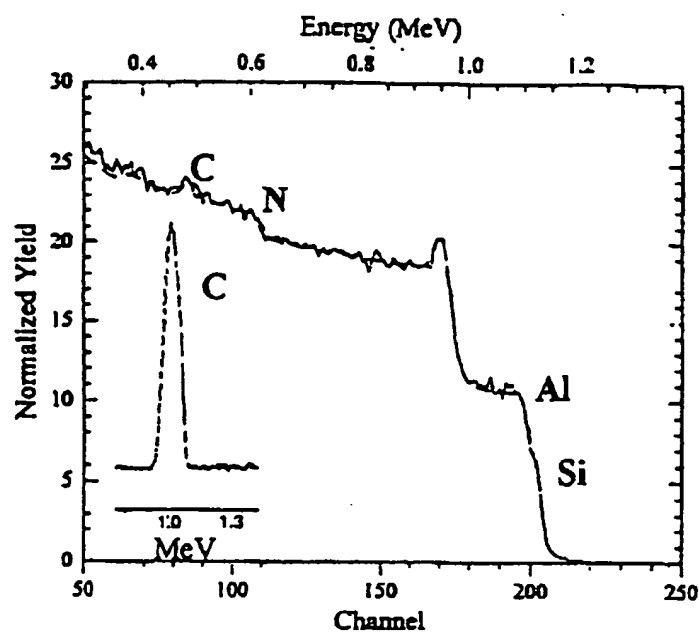


Fig. 8

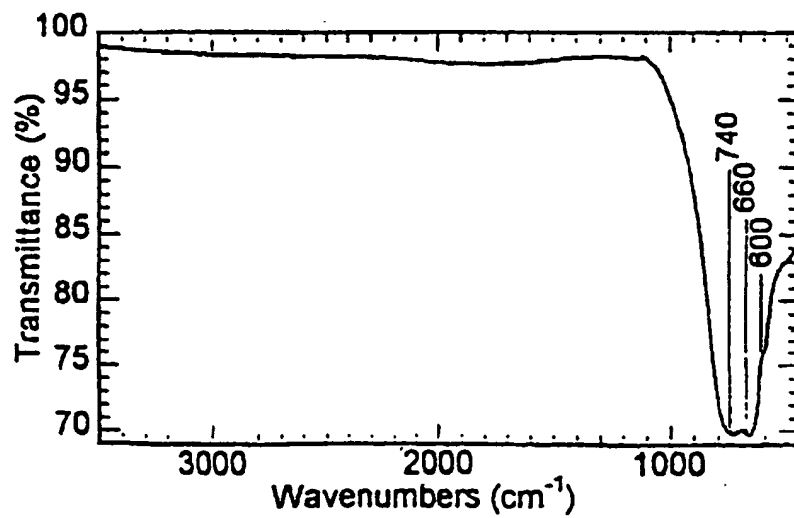


Fig. 9

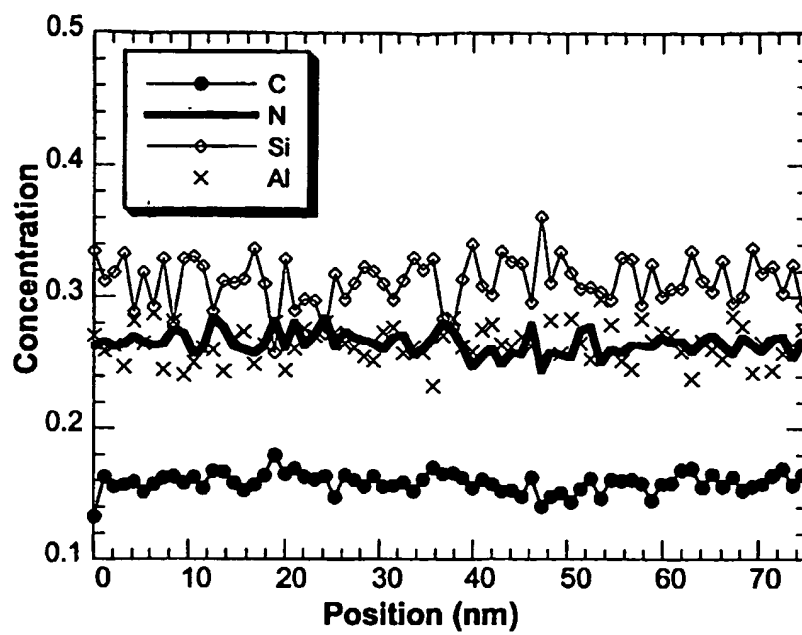


Fig. 10A

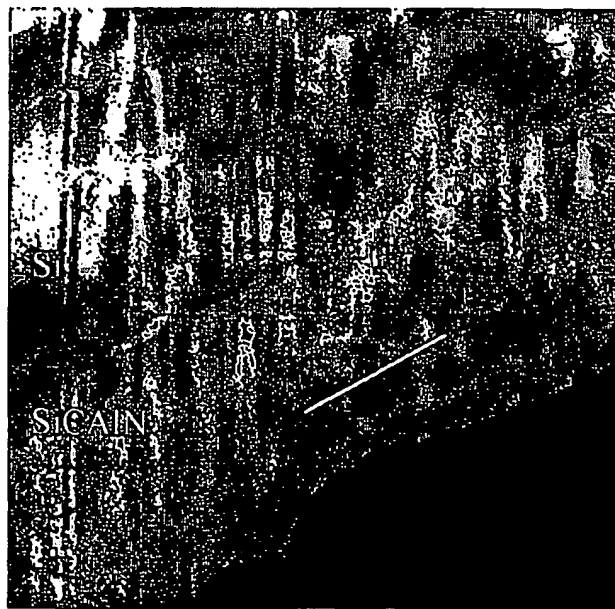


Fig. 10B

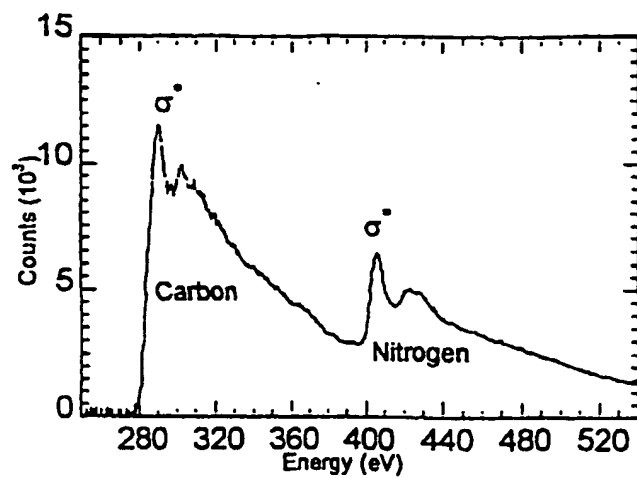
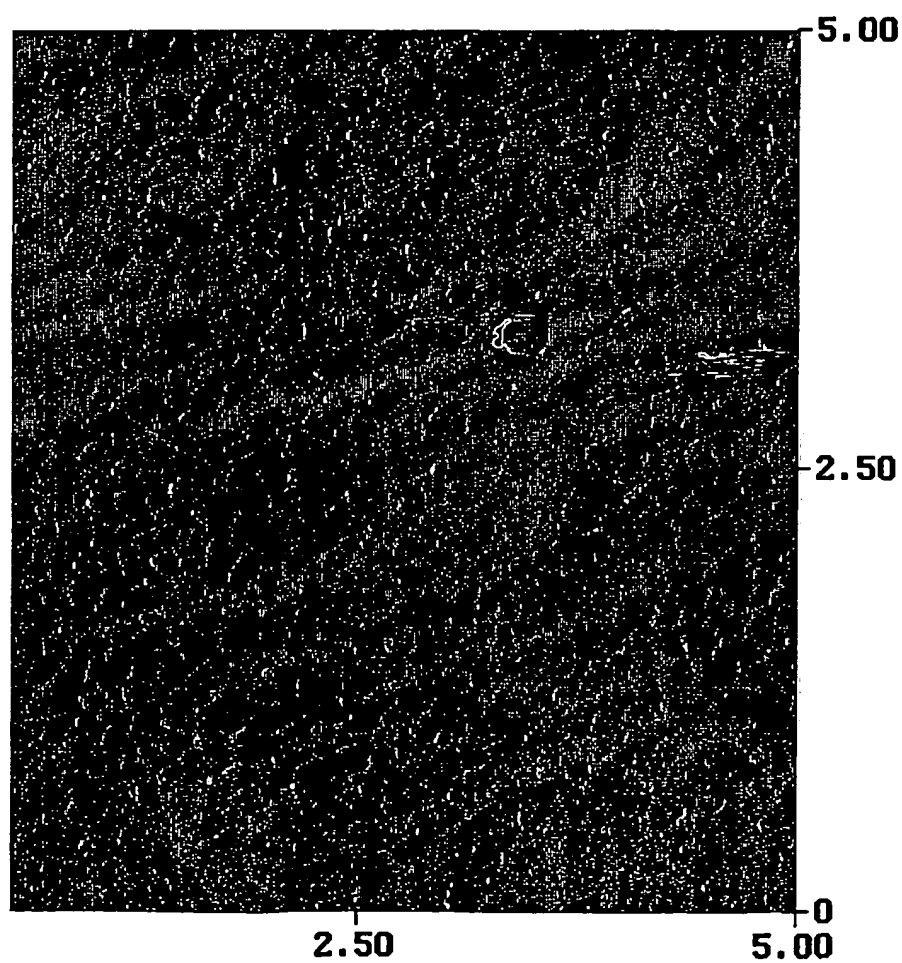
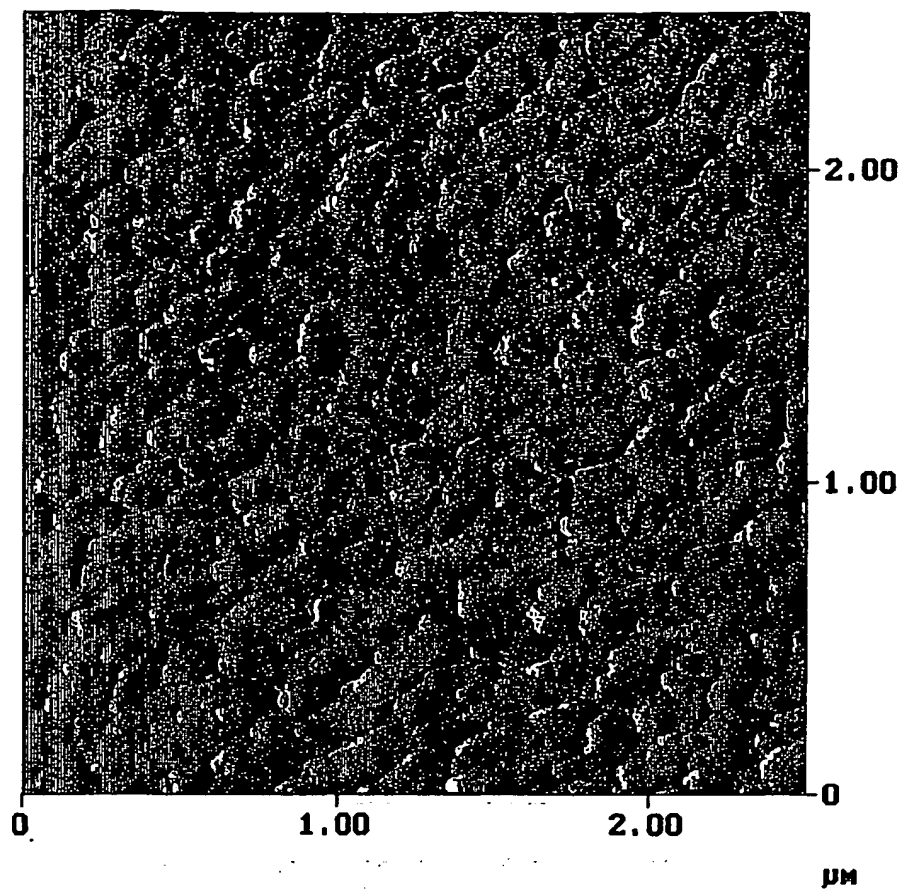


Fig. 11



Rms: 13.39 nm Ra: 2.84 nm μm

Fig. 12a
7/11



Rms: 6.48 nm Ra: 2.65 nm

Fig. 12b

10
↓

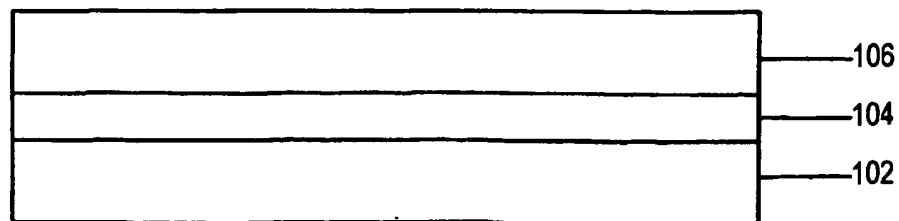


Fig. 13

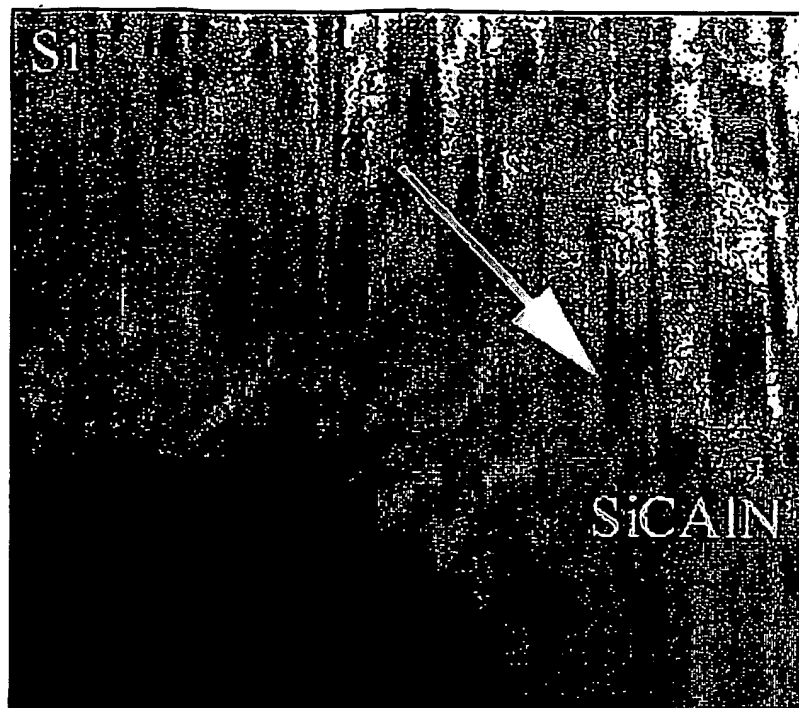
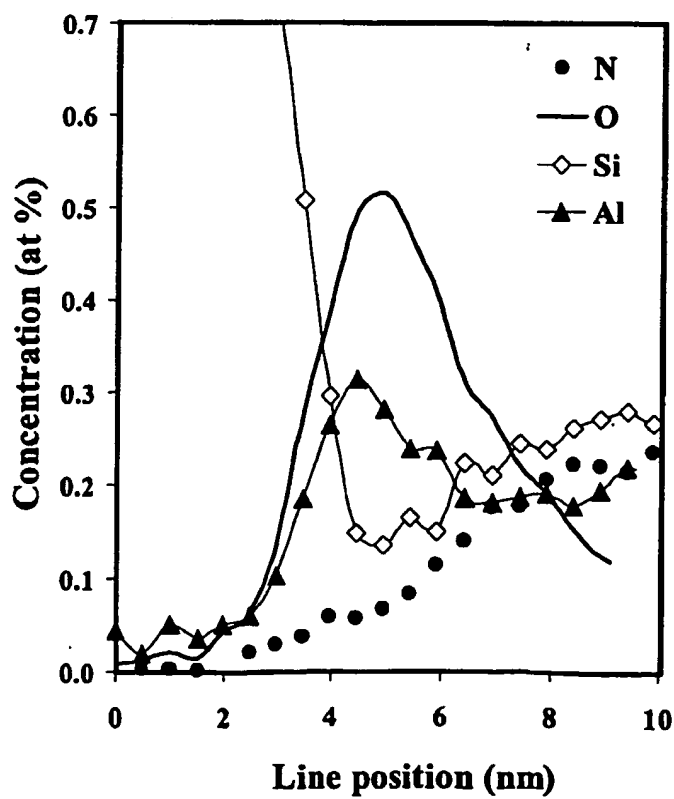


Fig. 14



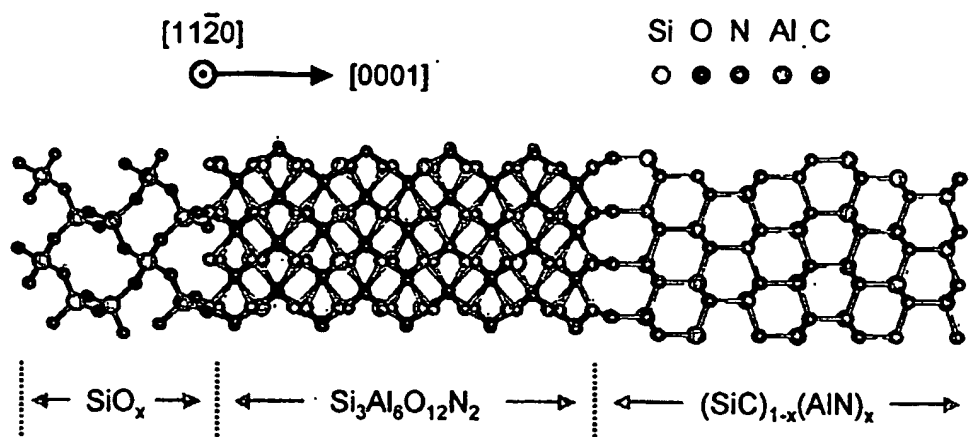


Fig. 16

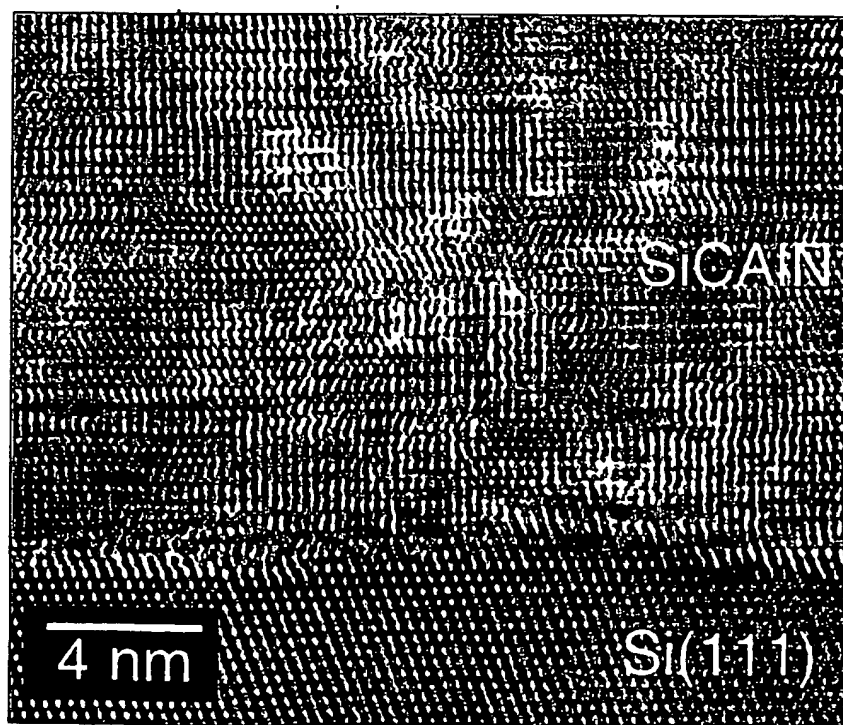


Fig. 17

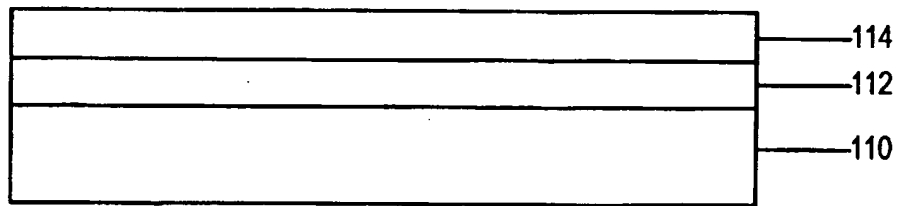


Fig. 18

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/33134

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C30B 25/00

US CL : 117/92

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 117/92, 84, 103, 108

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN, EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,952,111 A (SUGG et al) 14 September 1999 (14.09.1999), column 6 lines 30-40.	1-36
A	US 5,766,783 A (UTSUMI et al) 16 June 1998 (16.06.1998), all.	1-36
A	US 5,676,723 A (TANIGUCHI et al) 14 October 1997 (14.10.1997), column 10 lines 1-24.	1-36
A	US 6,201,342 B1 (HOBART et al) 13 March 2001 (13.03.2001), column 3 lines 20-49.	1-36
A	US 6,113,451 A (HOBART et al) 05 September 2000, (05.09.2000), column 3 lines 25-52.	1-36



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 February 2003 (26.02.2003)

Date of mailing of the international search report

20 MAR 2003

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Benjamin Utech

Telephone No. (703) 308-0661

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.